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Infrared investigation of binary silver borate glasses

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Abstract : Infrared spectroscopic investigation of binary silver borate glasses in the system $xAg_2O.(1-x)B_2O_3$ for various values of x ($0 \leq x \leq 0.77$) have been performed in order to understand the glass modifying properties of the Ag_2O. The I. R spectra show clearly the disappearance of boroxol rings and the formation, in a first step, of tetraborate groups and later of diborate groups as the oxide content increases. For high Ag_2O content, borate groups with non-bridging oxygen atoms are formed.

Keywords : Infrared spectra, borate glasses

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A growing interest has developed recently in borate glasses with Ag as a network modifying ion (NMI), following the technological applications of these materials with respect to the alkali borate glasses, especially as a basis for the preparation of fast ionic conductors [1,2].

In particular for silver borate glasses $xAg_2O.(1-x)B_2O_3$, extensive experimental evidence from Raman[3]. NMR[4] and Ultrasonic[5] measurements permitted the following structural model. At low concentration of Ag_2O ($x \leq 0.25$), the trigonal coordination of the boron is partially changed into tetrahedral, giving rise to the formation of BO_4 groups along with an increase of the network coherence. At higher concentration of Ag_2O ($x \geq 0.25$), the relative number of tetrahedrally coordinated boron ions tends to decrease and coherence breakdown occurs with the formation of non-bridging oxygens (N. B. O.).

The procedure followed for the preparation of glass samples has been described elsewhere [3]. The glasses were powdered, mixed with an appropriate amount of anhydrous KBr powder and then pressed at 10 tons load for 2 minutes for transmittance measurements in the region 600-4000 cm^{-1}. This procedure gave transparent pellet with about 2 wt% of glass. The spectra were recorded on Perkin-Elmer spectrometer (Model 681) in the region 600-4000 cm^{-1} where the instrumental resolution of about 2 cm^{-1} was achieved (Figure 1).

The role of Ag_2O in the silver borate glass system can be understood by a study of the change in its I. R spectra. The main observation is the growth of new bands in the region between 850–1120 cm^{-1} upon increasing the concentration of Ag_2O in the B_2O_3 matrix. At the same time, intensity changes of the 1200 and 1400 cm^{-1} bands are also observed. By

reference to the work of Krogh-Moe [6], it is widely accepted that the broad band in the region around 1200 cm^{-1} is attributed to B-O bond stretch of trigonal BO_3 units, while the bands in the region 850-1100 cm^{-1} arise from B-O bond stretching of tetrahedral BO_4 units.

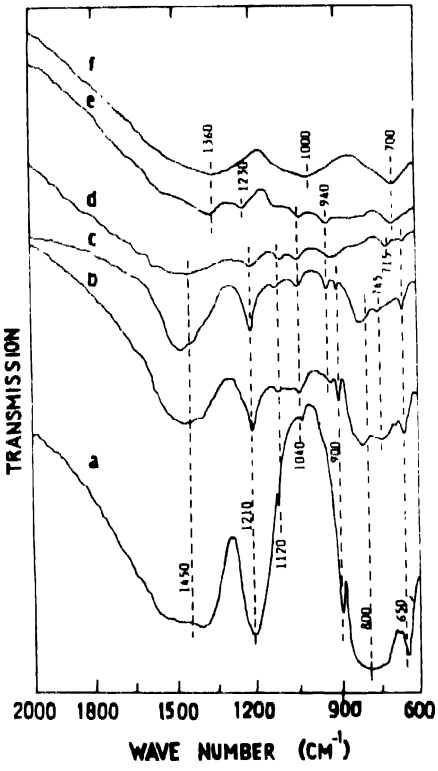
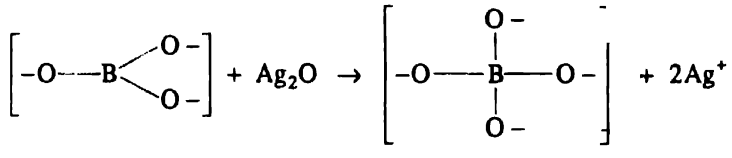
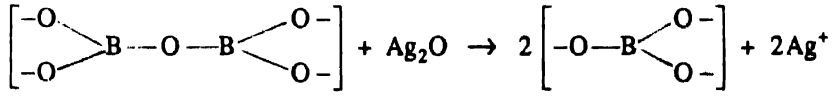


Figure 1. Infrared transmittance spectra of silver borate glasses in the system $xAg_2O.(1-x)B_2O_3$ for different values of x (a) 0 (b) 0.15 (c) 0.22 (d) 0.33 (e) 0.44 (f) 0.77.

These results are supported by the number of four coordinated boron atoms (BO_4) given by Bray *et al* [7] in NMR experiments. The modifying effect of the silver can be described by the equations:



(for low Ag_2O content)



(for high Ag_2O content)

The high frequency band envelope (1458 cm^{-1}, x = 0.10) which is due to stretching of B-O bonds of rings of various borate arrangements containing planar six membered borate groups, exhibits a compositional dependence. As the concentration of Ag_2O is increased, this band shifts to higher wavenumber 1488 cm^{-1} for x = 0.33 and then starts to shift to lower wavenumber and finally appears at 1360 cm^{-1} for x = 0.44 concentration. The spectrum of crystalline lithium pyroborate shows a band in this region, originating from asymmetric $>B-\bar{O}$ stretching of $B_2\bar{O}_5^4$ units. On this basis, we tentatively assign the 1360 cm^{-1} band to the presence of pyroborate units in silver borate glasses with high Ag_2O content. The shift of band around 1450 cm^{-1} with concentration of Ag_2O is shown in Figure 2 while the variation of the integrated intensities of bands around 1450 and 1200 cm^{-1} with concentration of Ag_2O are shown in Figure 3.

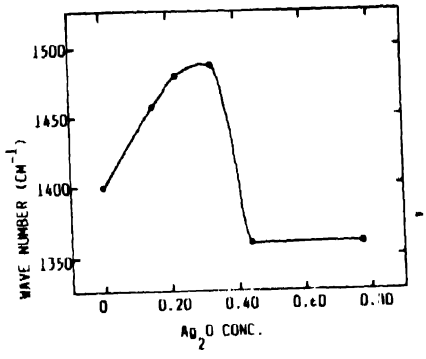


Figure 2. Shift of band around 1450 cm^{-1} with concentration of Ag_2O.

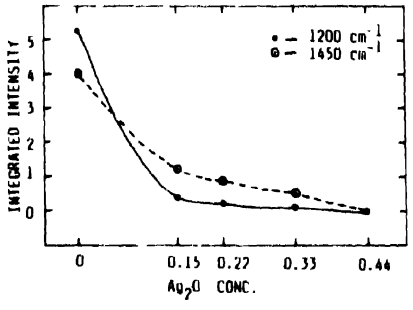


Figure 3. Integrated intensity of band around 1450 and 1200 cm^{-1} with concentration of Ag_2O.

More interesting results on the typical borate units, constituting the glass network have been obtained by analysing the bands in the region 850-1120 cm^{-1}, which shows a fine structure comprising of four components. By comparison with the spectra of polycrystalline compounds [8] having the same formula, one component at 1000 cm^{-1} corresponds to B-O bond stretching of BO_4 units in diborate polycrystals [6], while the others near 900, 940 and 1040 cm^{-1} correspond to the same vibration but in tetraborate units. The observed evolution of the band shape with x is caused by a change in the relative number of these two different borate groups. At low Ag_2O content, BO_4 units are preferably contained in tetraborate groups. The smoothing of the band and the position of its maximum at about 1000 cm^{-1} indicates its transformation into diborate rings with the increase in x.

The region 600-700 cm^{-1} is also of considerable interest. The band at 655 cm^{-1} decreases in intensity with addition of Ag_2O content and finally disappears at x = 0.44 concentration. Pentaborate groups of crystalline (α – and β–$K_2O.5B_2O_3$) show bands at 650 and 625 cm^{-1} respectively, while tetraborate groups do not show bands in this region [8]. Thus it can be concluded that 650 cm^{-1} band denotes the presence of pentaborate groups. Schematic representation of different borate arrangements is shown in Figure 4.

Similar results have been deduced from NMR measurements [9]. They are also in good agreement with the variation of glass transition temperature (T_g) and density, with x as reported by Button *et al* [10]. Effectively, the model proposed here for the boron-oxygen network can describe these effects satisfactorily. In the first step, the formation of BO_4 groups in tetraborate units and diborate units gives an increase in linkage of the network which produces the increase observed in the temperature T_g and density. In the second step, with further increase of silver oxide content, the diborate units are destroyed to form BO_3 triangles with non-bridging oxygen atoms. This corresponds to a decrease in the linkage of the network which causes a decrease in the above two parameters.

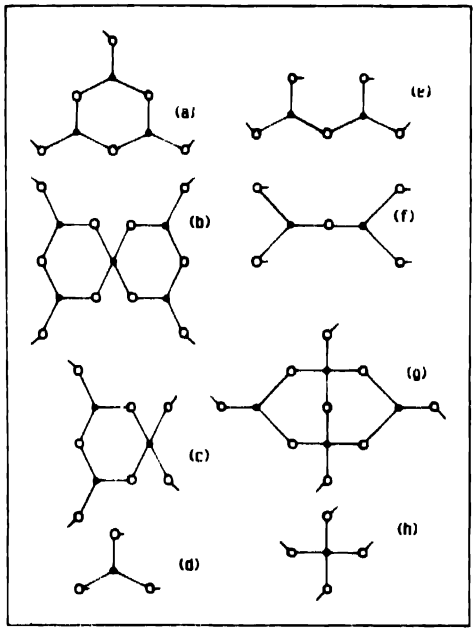


Figure 4. The schematic representation of different borate arrangements.

(a) boroxol unit (b) pentaborate unit (c) triborate unit (d) orthoborate unit
(e) metaborate unit (f) pyroborate unit (g) diborate unit (h) loose BO_4

Solid circles represent boron atoms, open circles oxygen atoms. An open circle with a negative sign indicates a non-bridging oxygen.

Acknowledgments

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